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No. 78

PROPERTIES OF THE CALCIUM SILICATES AND CALCIUM ALUMINATE OCCURRING IN NORMAL PORTLAND CEMENT

BY

P. H. BATES, Chemist

and

A. A. KLEIN, Assistant Physicist

Bureau of Standards

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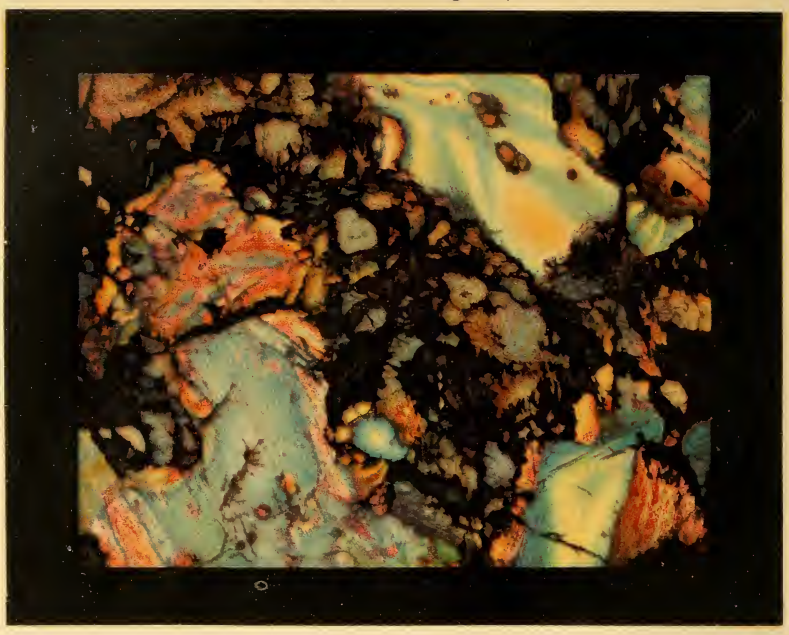

FIG. 2.—*Thin section of dicalcium silicate examined with crossed nicols*

Note the irregular outline of the grains, also the brilliant interference colors. In the case of the tricalcium silicate those grains not in extinction (appearing black) would be white to yellowish gray. Compare with Fig. 6 where the same section is shown in black and white. (X190.)

FIG. 3.—*Thin section of dicalcium silicate, containing approximately 1 per cent Al_2O_3 (burn 35), examined with crossed nicols*

Note the distinct outline of grains, cemented together by $3CaO.Al_2O_3$ which appears black. Compare with Fig. 2, bearing in mind the difference in Al_2O_3 content; also compare with Fig. 7 where this is shown in black and white. (X90.)

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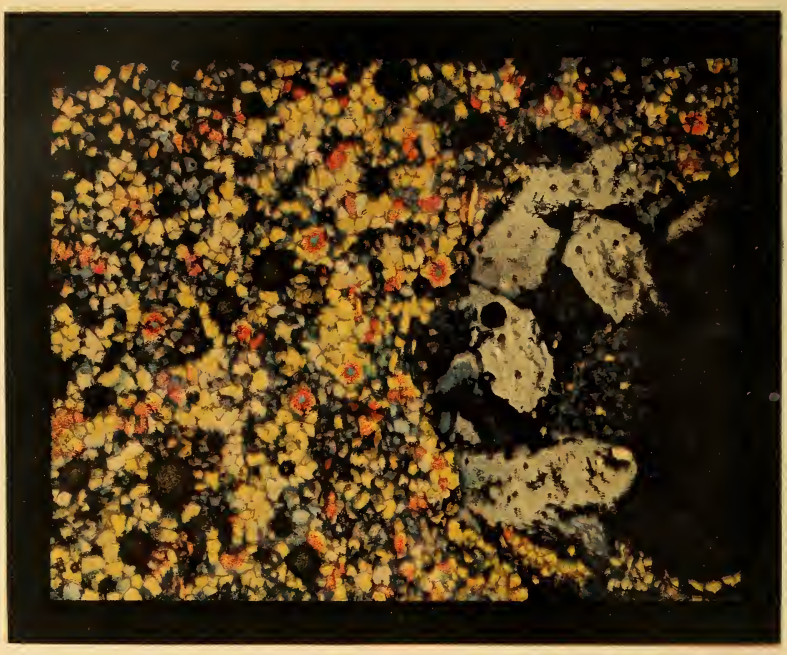

FIG. 4.—*Thin section of burn 38 examined with crossed nicols*

Shows some large-grained $3CaO.SiO_2$ (appearing gray) at the one side of the section on the edge of a void (appearing black). The remainder of the section is very fine-grained $2CaO.SiO_2$, readily distinguished from the $3CaO.SiO_2$ by the color. This segregation of $3CaO.SiO_2$ is very frequently noted in commercial Portland cement clinker. Compare with Fig. 8, where the same is shown in black and white. (X 190.)

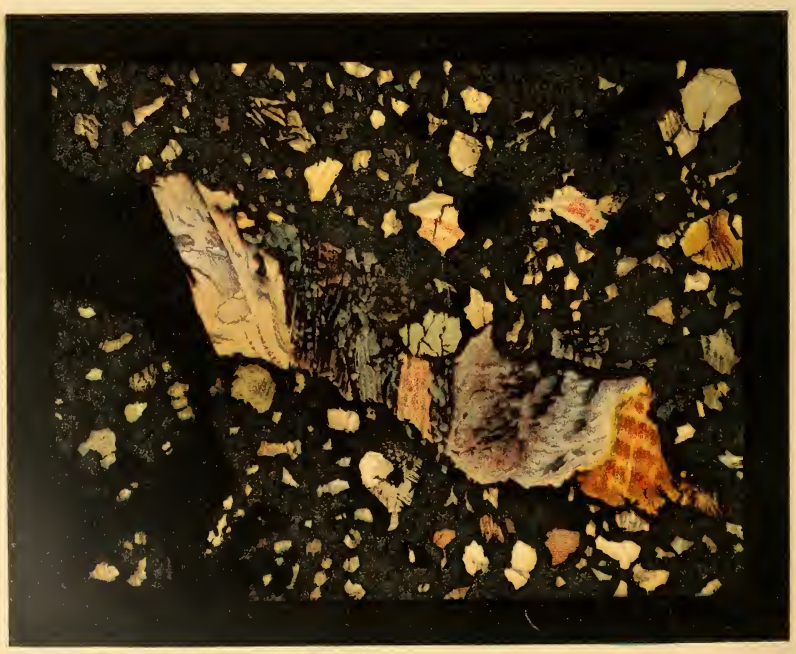

FIG. 5.—*Thin section of a one-year briquette of $2CaO.SiO_2$*

Shows a void partially filled with $Ca(OH)_2$, extending almost entirely across the field. The completely hydrated silicate appears black, the unhydrated or partially hydrated appears in yellow and brown irregular grains throughout the field. Compare with Fig. 15, where the same is shown in black and white. (X 90.)

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PROPERTIES OF THE CALCIUM SILICATES AND CALCIUM ALUMINATE OCCURRING IN NORMAL PORTLAND CEMENT

By P. H. Bates and A. A. Klein

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I. INTRODUCTION

As it has been shown within a comparatively few years [1] that the main constituents of Portland cement of normal composition and normal burning are tricalcium aluminate ($3CaO.Al_2O_3$), tricalcium silicate ($3CaO.SiO_2$), and the beta form of dicalcium silicate ($2CaO.SiO_2$), it becomes a matter of considerable importance to study the physical properties of these compounds, alone and mixed in various proportions. Of the various physical properties usually demanded of hydraulic cements, those of special importance are the strength developed by hardening (or hydrating) and the rate of acquiring this strength. Consequently, in the present investigation, the time of set; tensile

[1] Preliminary Report on the Ternary System, $CaO.Al_2O_3.SiO_2$, A Study of the Constitution of Portland Cement (Shepherd, Rankin, and Wright), Jour. Ind. and Eng. Chemistry, 3, pp. 211–227, 1911; The Ternary System, $CaO.Al_2O_3.SiO_2$ (Rankin and Wright), Amer. Jour. Science, 39, January, 1915; The Constitution of Portland Cement (Bates), Concrete and Cement Age (Cement Mill Section), 2, pp. 3–4, 1913; The Constitution of Portland Cement Clinker (Rankin), Jour. Ind. and Eng. Chem., 7, p. 466, 1915.

strength in the form of neat and 1:3 standard Ottawa sand briquettes at the end of 24 hours, 7 days, 4, 13, 26, and 52 weeks; and the amount of hydration at the end of the above-mentioned periods were determined by both chemical and microscopic methods on the above-mentioned compounds when used alone, when mixed with approximately 3 per cent plaster of Paris, when mixed with one another in about the proportion in which they occur in normal Portland cement, and when mixed in these same proportions with the addition of 3 per cent plaster of Paris. There was also a short series of burns made in a stack furnace, wherein the silica, lime, and alumina were burned together in

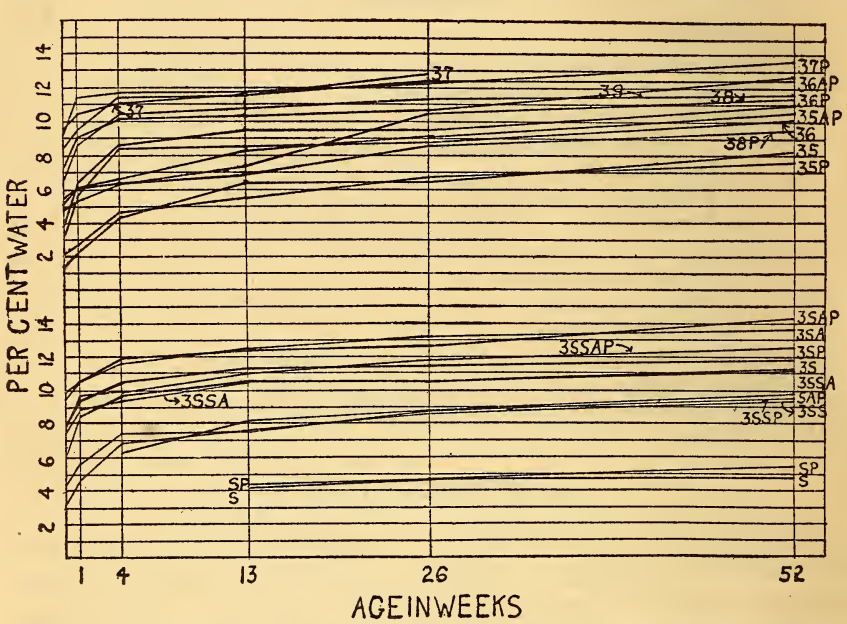

FIG. 1.—*The percentage of water of hydration of the burns at the various periods*

about the proportion in which they existed in the above-mentioned mixtures, thus obtaining cements in which the components had all been burned together, as opposed to the mixture when they had only been ground together.

While in this investigation only the three compounds mentioned were used, it must not be assumed that these are the only hydraulic compounds which can result from either the binary or ternary combination of silica, lime, and alumina. Preliminary work in the laboratory has shown that in this system there are a number of compounds which have the property of hardening to strengths, at early periods, considerably beyond the strength developed by Portland cement, but as these do not

occur in this latter material and as this paper is confined to those that do so occur, they are not included.[2] In addition to the three compounds included in this investigation, there are four others which may occur, namely, the 5:3 calcium aluminate ($5CaO.3Al_2O_3$), monocalcium aluminate ($CaO.Al_2O_3$), a ternary compound ($2CaO.Al_2O_3.SiO_2$), and lime (CaO). These, however, occur only in cements of abnormal composition or of abnormal burning, and are consequently not considered.

II. METHOD OF PREPARATION OF COMPOUNDS

The difficulties encountered in making these compounds (especially the silicates) in small quantities, when approximately pure, were so great that, since it was desired to obtain as much as 30 pounds of material, it was deemed advisable to discontinue the attempts, but, on the other hand, to work toward as low an amount of impurity as possible. In the case of the silicates, preliminary work showed so much difficulty, when using a fairly pure high-calcium limestone and a very pure grade of flint, in obtaining a material free from the gamma form of the dicalcium silicate that a search was made for a "mineralizer" (or so-called mineral catalyzer) which would bring about the more ready formation of the desired silicate without that disturbing factor. For this purpose the use of alumina was prohibited, since it was very important to have the silicates as free from this as possible, because it has been found to affect their properties to a marked degree even when present in small amounts.

A study of the addition of small amounts of the oxides of nickel, vanadium, molybdenum, tin, magnesium, potassium, tungsten, boron, and chromium to mixtures of silica and lime, in the molecular proportion of one of the former to two of the latter, and burning the mixture at a temperature of 1550° C for one hour, showed that reversion to the gamma form of the dicalcium silicate was prevented only in the case of the oxide of boron and the oxide of chromium, the former being used in the form of boracic acid and the latter as the green oxide. These substances in amounts of less than 1 per cent entirely prevented the reversion of mixtures in the ratio of 2CaO to SiO_2 to the gamma form with one heating for an hour at 1550° C. Therefore, in this investigation two burnings of the dicalcium silicate were made, one with the

[2] This statement is made to correct a too common impression that in the system Silica-lime-alumina only those compounds which occur in Portland cement have the property of hardening on the addition of water. The preliminary work mentioned above on all the compounds of this system is being continued on a larger scale, and at a later date a separate paper, covering the compounds not included in this paper, will be issued.

addition of the boracic acid and the other with the green oxide of chromium. The former at 1550° C seemed to have approached a little more closely to the fusion point than the latter, the burned material being a hard glistening white cellular mass; when the oxide of chromium was used, a rather soft mottled-green material was obtained. The optical examination of this and the other burns is given in Table 1. (See also Figs. 2 and 6.)

In preparing the tricalcium silicate much more difficulty was encountered. The first burnings with the addition of either the boracic acid or chromium oxide produced a material which dusted on cooling to gamma dicalcium silicate and free lime. A second burning of the dusted material gave a similar result, though not to quite as marked a degree. The material was then reground and reburned. The reduction in the amount of dusting was very marked, and on grinding the material and adding water it set to a mass which in the course of 24 hours expanded to disintegration. A fourth reburning of the same material gave a product which dusted but slightly and showed in the undusted parts considerable amounts of beta dicalcium silicate and free lime, also an appreciable amount of the tricalcium silicate. This, when ground, hardened with water and did not show any signs of disintegration within 24 hours. It was reburned a fifth time, producing a material which did not dust and was largely tricalcium silicate, though beta dicalcium silicate and free lime were noted. When ground, it hardened on the addition of water, and when subjected to an atmosphere of steam for four hours (at the end of 24 hours after gauging with the water) it showed no signs of disintegration. It was, however, reburned a sixth time, the resulting product being very largely tricalcium silicate. The results of its optical examination are shown in Table 1. (See also Figs. 4 and 8.)

The usual trouble of making tricalcium aluminate was encountered, namely, the use of too high a temperature, resulting in a product which was $5CaO.3Al_2O_3$ plus free lime. The tricalcium aluminate is not stable at its melting point, decomposing as noted above. While its melting point is known, the melting point of the material used, which contained impurities, was not known; consequently, while a temperature about 50° C lower than the melting point of the pure compound was used, it was still too high. On regrinding and reburning at a temperature of about 1350° C for several hours, a very satisfactory compound was obtained, as can be seen in Table 1, from the results of the optical examination.

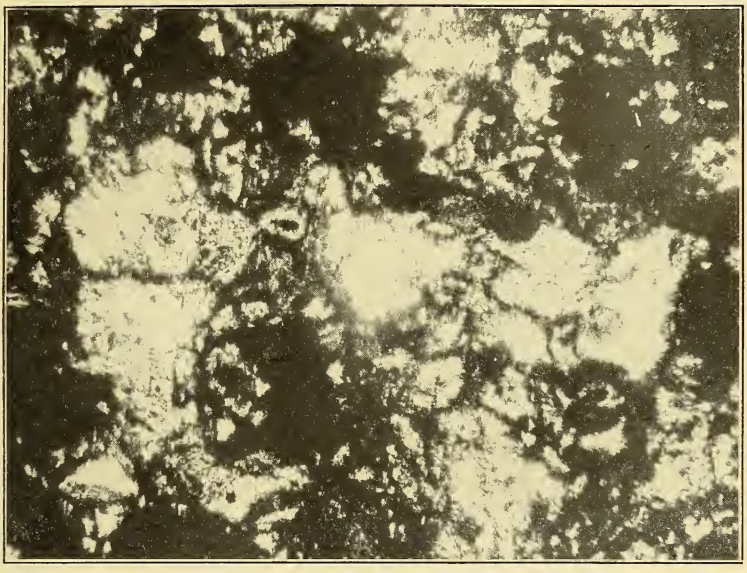

FIG. 6.—*The same section as figure 2 (2CaO.SiO_2 shown with crossed nicols) but reproduced in black and white* (×90)

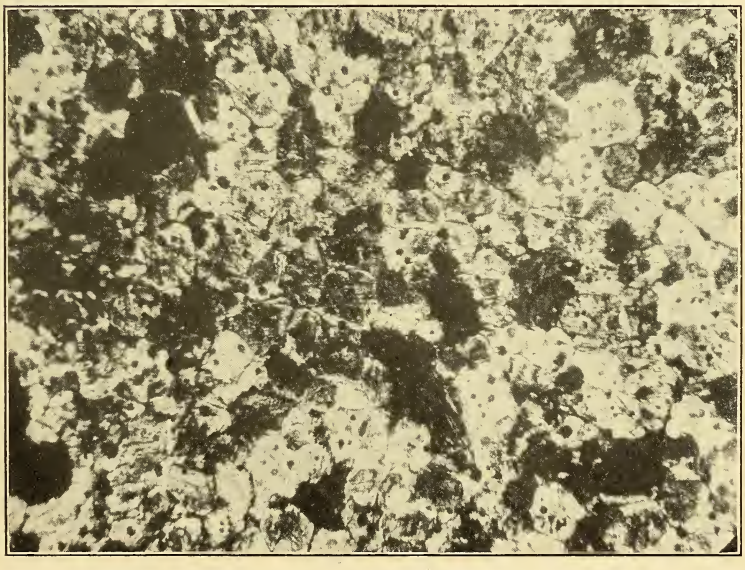

FIG. 7.—*The same section as figure 3 (burn 35 shown with crossed nicols) but reproduced in black and white* (×90)

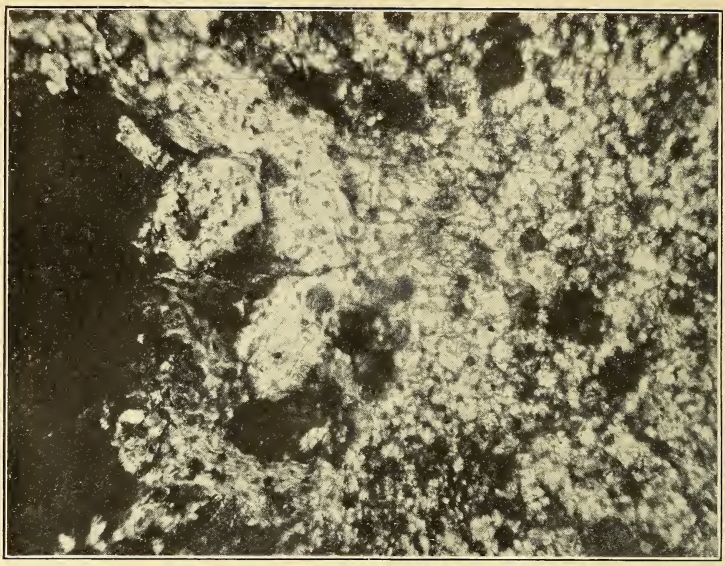

FIG. 8.—*The same section as figure 4 (burn 38 shown with crossed nicols) but reproduced in black and white* (×190)

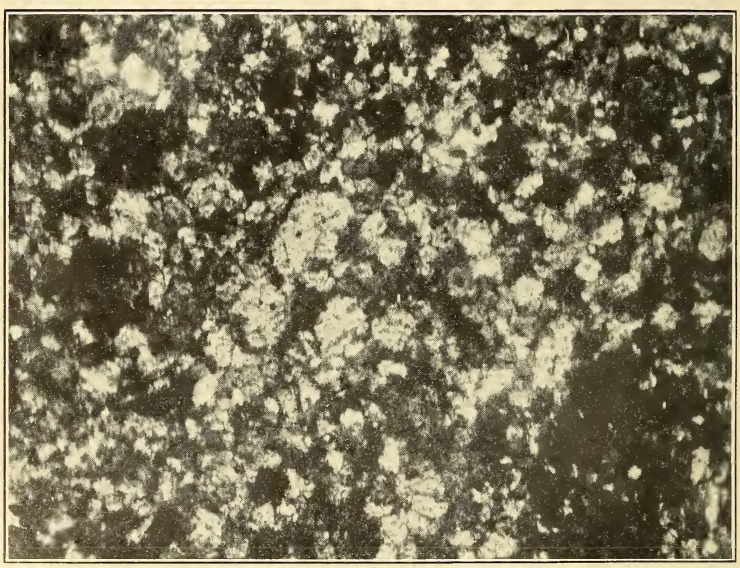

FIG. 9.—*Thin section of burn 36, very largely* $3CaO.SiO_2$, *examined with crossed nicols*

If reproduced in color it would be but little different than as shown, appearing black, if in the position of extinction, to grayish white. Note the lack of definite outline when compared with burn 35 ($2CaO.SiO_2$ containing about the same amount of Al_2O_3). (×90.)

In addition to the above, there was burned a dicalcium-silicate mixture of the limestone and flint to which approximately 1 per cent of alumina and one-quarter per cent of boracic acid were added. These two additions were also made to a tricalcium-silicate mixture of the same flint as used above, but another limestone which, while of equal purity so far as silica and alumina were concerned, contained about 50 per cent more magnesia. The effect of these additions and impurities was very marked in permitting the ready burning of a satisfactory product, only two burnings being necessary. These two burnings (hereinafter referred to as "35" and "36") gave a dicalcium and a tricalcium silicate, respectively, of greater impurity than the two first mentioned and were made for the purpose of determining the effect of the increased alumina on the properties of these compounds. (See Figs. 3, 7, and 9.)

Three further burnings, 37, 38, and 39, were also made of mixtures containing silica, lime, and alumina in such proportions as to give cements corresponding in composition to that obtained by the mechanical grinding together of the three pure compounds. These mechanical mixtures were made, first, in the ratio of 81 parts of dicalcium silicate to 19 tricalcium aluminate, giving a material analyzing, on the basis of pure compounds, 28.3 per cent SiO_2, 7.2 per cent Al_2O_3, and 64.5 per cent CaO; second, in the ratio of 81 parts of the tricalcium silicate to 19 tricalcium aluminate, giving a material analyzing 21.3 per cent SiO_2, 7.2 per cent Al_2O_3, and 71.5 per cent CaO; and third, in the ratio of 40.5 tricalcium silicate, 40.5 dicalcium silicate, and 19.0 tricalcium aluminate, figures which correspond to 24.8 per cent SiO_2, 7.2 per cent Al_2O_3, and 68.0 per cent CaO. The first of the above would correspond to the extreme limit in a high-silica, low-lime, Portland-cement clinker; the second to a low-silica, high-lime one, and the last to a normal clinker.[3] The last three burnings were made to determine whether it was possible to obtain a product having hardening and other physical properties similar to that of another product of like composition, but obtained by the mechanical mixing of the constituents after their separate burning; in other words, to find if it be possible to reproduce any cement, in which the amount of the various constituents had been determined, by the simple grinding together of these constituents, previously separately burned, in the proportion in which they were found to exist in the cement.

[3] These figures refer to clinker analyses and not finished cement analyses, which would show also the added plaster, absorbed water, and carbon dioxide.

III. GRINDING AND MIXING OF THE COMPOUNDS

In Table 2 is shown the proportions in which the various separately burned constituents were mixed together, and the reference marks by which the cements so prepared were identified. Hereafter, in order to condense as much as possible, these reference marks will be used when referring to a particular mix, instead of giving the complete composition of each. Furthermore, as in the case of the burns of the purer compounds, where two separate burns were made, one containing boracic acid as a "mineralizer" and the other chromium oxide, so here also there were two classes of mixtures of similar composition but containing the different "mineralizer." Those made from the burnings in which boracic acid was used will be referred to as "white;" those in which the chromium oxide was used as "green."

The mixing was done in a porcelain ball mill, using only a few small pebbles, the purpose being only to mix and not to grind, since the latter operation had been performed on each burn separately. While possibly this method did not give as intimate a mixture as the grinding together would have done, yet the mixing in this manner was undoubtedly sufficiently intimate after the mills had been run three hours.

The grinding of the burns by means of pebbles in a porcelain mill was not as satisfactory as was desired, the uniformity of fineness desired for each not having been obtained. Whereas a product showing a fineness of about 80 per cent through a 200-mesh sieve was wanted, this was exceeded in too many cases, owing largely to a difference in the degree of vitrification of the material and a lack of experience in grinding such small quantities of material. The fineness of the different burns were as follows:

	Percentages passing—	
	100-mesh sieve	200-mesh sieve
$2CaO.SiO_2$ (white)	99.2	86.4
$2CaO.SiO_2$ (green)	98.4	78.8
$3CaO.SiO_2$ (white)	98.4	84.8
$3CaO.SiO_2$ (green)	94.4	77.6
$3CaO.Al_2O_3$	99.4	85.6
35	98.0	92.0
36	97.6	89.2
37	Tr.	99.0
38	97.4	82.4
39	99.2	89.8

IV. TIME OF SET OF THE MIXED COMPOUNDS

Possibly of as much importance as the time of set was the nature of the gauged mass when kneaded with water, especially in regard to the degree of plasticity developed and the relative amount of heat evolved. These two items as well as the time of set and amount of water to form a mass of normal consistency (by the ball method) are summarized in Table 4. More detail than can be readily placed in tabular form is necessary in order to clearly understand these various phenomena, consequently each of the compounds will be discussed at some length separately as to the immediate effect produced upon them by kneading with water alone and when mixed together in the various proportions mentioned before.

1. TRICALCIUM ALUMINATE

This compound can not be kneaded with water by hand. The addition of water results in the immediate hydration, accompanied by the evolution of so much heat that the mass boils. The reaction is even more rapid, and apparently as much heat is evolved as in the case of the hydration of normally burned quicklime. In the latter case there is not much likelihood of incomplete hydration, but in the case of this aluminate, even when used in the powdered form, it quickly agglomerates into balls which hydrate on the exterior to hard masses which prevent the penetration of the water to the interior; consequently, large masses of unhydrated material are present. Therefore, in gauging this material with water, an amount of water equal to about 40 per cent of the weight of the compound to be used was placed in a mortar and the compound added gradually accompanied by continued grinding with the pestle. About one minute after adding all of the compound it was necessary to add about 10 per cent more water to reduce the mass to normal consistency. This mass was even then full of small grains of material hydrated only on the exterior.

No time of set was obtained. Time-of-set test pieces, when placed in the damp closet, seemed to stiffen considerably in the course of a day, enough to sustain the small Gilmore needle at the end of three hours; at the end of three days they would sustain the large Gilmore needle, but if then examined under the surface they were found to be quite soft, so that the entire mass could be kneaded in the hand (without any further addition of water) to as plastic a mass as it was at first. This ability of the aluminate to work up into a plastic mass, at the end of long periods

after its first having been gauged with water, is very striking; and furthermore, as will be noted later, it confers this property upon the cement which is obtained by mixing it with the silicates. This property of acquiring plasticity, to a certain degree, after acquiring an initial set has been frequently [4] noted in the testing of Portland cement. This return to a plastic mass will take place in Portland cements of normal composition which do not contain much of the tricalcium silicate. The presence of this latter compound, which, as will be shown later, hydrates rapidly, would mask this phenomenon.

The addition of plaster of Paris in amounts equal to 3 or 10 per cent of the weight did not make any marked difference in the amount of heat evolved or in the other general properties of this aluminate which result when it is mixed with water. The amount of water necessary to make either the aluminate alone or the aluminate with plaster addition workable was greatly in excess of that usually required by cement. Thirty per cent of water, which would be a large amount for a normal cement, was hardly sufficient to make the mass appear more than damp. The evolution of heat was much localized in such a case, resulting in a very high temperature, which evaporated a considerable amount of the water; the use of 50 per cent gave a much more uniformly wet mass and one that could be molded.

2. DICALCIUM SILICATE

The kneading of the dicalcium silicate with water produced no more plasticity than would have resulted from the substitution of ground quartz of equal fineness for the silicate. There was no appreciable evolution of heat. There was an apparent set obtained, but this was really a drying out and could hardly be called a true set resulting from hydration. When the plaster had been added to this silicate a result only slightly different was obtained; possibly more plasticity was produced, but the time of apparent set was not changed.

The addition of tricalcium aluminate to dicalcium silicate produced quite a marked change, noticed immediately by a rapid and strong evolution of heat, which produced an initial set before the test pieces could be molded. Consequently, the initial set noted in Table 4 is the initial set of the material regauged *without the addition* of any more water. An initial set of 22 minutes was

[4] McKenna, Metallurgical and Chem. Eng., Vol. X, No. 2, p. 83; Burchartz, Eng. Record, 1909, p. 661; Garry, Concrete and Constructional Eng., 1906, p. 356; Bates, Trans. Am. Cer. Society, Vol. XVI (1914), p. 551.

obtained when this mixture was kneaded for one-half a minute and immediately made into a test piece, but longer kneading reduced the initial set to a flash. If this mass after the flash set, when it seemed quite hard, was kneaded further, it was reduced to a consistency much thinner than that required for normal consistency. Of course this condition was brought about entirely by the presence of the aluminate, as it was noted very markedly in the investigation of this compound alone, but was lacking entirely by the dicalcium silicate. There was also a marked increase in the plasticity and lack of granularity in the mortar resulting from the mixture of these two compounds.

The addition of 3 per cent of plaster to the mixture of dicalcium silicate and tricalcium aluminate produced a very quick initial and final set. This appeared also to be more of the nature of a true set, and not due to a drying out produced by excessive heat evolution but rather to a hardening due to hydration. The heat evolved was less than when plaster was not used, but still marked and undoubtedly was sufficient to cause the early final set by accelerating the chemical process of hydration. The mortar was also marked by a decided increase in plasticity and smoothness.

The mixes in which dicalcium silicate was the only silicate present produced pats which would not be considered sound after the steam treatment. There was, with one exception, no sign of cracking or warping, but the pat gave a very dull ring. One pat was disintegrated. The entire behavior of the pats was due, however, to lack of sufficient strength and sufficient density to give them a normal appearance. The results do not show lack of soundness as that term should be understood, which produces disintegration, due to expansive force produced by the hydration of abnormal constituents, usually free lime.

3. TRICALCIUM SILICATE

This compound when gauged alone with water had all the properties of normal Portland cement, excepting a slightly inferior plasticity. When it contained 3 per cent of plaster, it even had the plasticity of Portland cement, but its initial set was considerably quicker. The addition of tricalcium aluminate produced a very plastic mass, which also gave off much heat and produced a very quick set; plaster reduced the heat evolved and slowed up the initial set. The mixture of the silicate and the aluminate showed, but to a very slight degree, the property of being regaugable to a plastic mass after the initial set without the addition of

water. It will be remembered that this was very characteristic of the aluminate alone and also when mixed with the dicalcium silicate. Apparently, in the present case, the hydration of the tricalcium silicate has proceeded to such an extent at this short period that such regauging is impossible unless more water is added.

The mixture of the two silicates resembled Portland cement after gauging with water, though it was decidedly more sandy. The addition of plaster to this mixture increased the plasticity and again decidedly reduced the time of set. The addition of the tricalcium aluminate reduced the time of initial set to a flash set and also reduced the final set somewhat more than one-half and was accompanied by a decided evolution of heat; it also made a very plastic workable mortar. The addition of aluminate and plaster reduced the heat evolved somewhat, increased the time of initial set, but reduced the final set and also produced a very workable plastic mortar. All pats were very hard and gave a very good ring, except the mixture of the two silicates and aluminate. Here, again, the effect of the aluminate can be readily traced. It produced a flash set, accompanied by so great evolution of heat that the final set was really a drying out. Consequently, the pat had not hydrated sufficiently in 24 hours to have density enough to give a proper ring.

4. BURNS 35 TO 39

It will be recalled that there were five other burns used, one of which was of the composition of the dicalcium silicate containing about 1 per cent alumina, another of the composition of tricalcium silicate containing 1 per cent alumina, and the other three approximately of the composition of mixes SA, 3SA, and 3SSA. A comparison of the results from these burns, shown in Table 4, with the results from the mixes is very striking. Thus, note the similarity between 35 and S, 35P and SP, and 35AP and SAP. At the same time the effect of the increased alumina in 35 is noticeable, particularly in reducing the time of set. Burn 36 and the mixes produced from it show very clearly its relation to the tricalcium silicate. Burn 37, approximating 3SA in its composition, exhibits many of the latter's properties, and when plaster is added to it, it exhibits the same results as were obtained by adding plaster to 3SA, an increase in the time of initial set and but slight change in the time of final set. Burn 38, approximately SA in its composition, is not so close in its properties as would be expected from the other similar relations shown. This is due to

the nature of the dicalcium silicate and tricalcium aluminate when produced in the same burn; they do not show the distinctly granular form or individuality of crystalization that characterizes the presence of the tricalcium silicate. They are invariably present together without any distinct outline and fused into one another; consequently, after grinding, the dicalcium silicate, being greatly in predominance and fused around the aluminate, prevents the ready access of water to the latter and thereby increases the time of set of such a burn as 38 over that shown by such a mix as SA, and also prevents the evolution of heat. (It should be borne in mind that the time of set for SA, shown in Table 4, is the time of the regauged material.) The resemblance between 39 and 3SSA is more marked, but again the effect of the dicalcium silicate in the burn is shown by its preventing the quick hydration of the aluminate and thereby preventing the evolution of heat.

Before concluding under the general topic of time of set it would be well to summarize.

1. The tricalcium aluminate hydrates so rapidly and with an evolution of so much heat that it can not be made into test pieces except with large quantities of water. As much as 10 per cent of plaster does not reduce the rapidity of this reaction.

2. The dicalcium silicate hydrates so very slowly that a true time of set can hardly be said to be obtained. It does hydrate and does set, but this is a matter of days and not hours, and consequently the time of set, as now determined, can not be said to be obtainable.

3. The mixtures of dicalcium silicate and tricalcium aluminate have the properties of the aluminate.

4. The tricalcium silicate approaches very closely Portland cement of normal composition.

5. The mixtures of the tricalcium silicate and dicalcium silicate have the general properties of the former.

6. The mixtures of tricalcium silicate and tricalcium aluminate show the ability of the former to materially modify the properties of the latter.

7. Mixtures of the two silicates and the aluminates show the effect of the presence of the aluminate more markedly than any of the other constituents.

8. Burns (Nos. 35–39) of a composition approximately that of certain mixes (SA, 3SA, 3SSA, etc.) have properties of a most striking resemblance to that of the mixes.

V. STRENGTH OF THE TEST PIECES

Of almost equal interest to the actual strengths developed was the matter of the nature of the fracture and the general question of denseness, particularly the increase of denseness at any period over the preceding one; all of these factors are shown condensed in Table 5.

This table gives the strength of all test pieces broken. The amounts of material available, unfortunately, did not allow of the making of more than two tensile test pieces for more periods than those shown, and while these are not as concordant as wished, yet the results do show the general properties of each compound very distinctly.

1. TRICALCIUM ALUMINATE

The results of the time of set of the tricalcium aluminate show certain properties of this compound which are corroborated by the strengths developed by it. It did not have the property of hardening under water; even if kept in the air for a year and then placed in water, it soon crumbled away. The addition of 3 per cent of plaster did not materially change it; 10 per cent gave test pieces which had practically no gain in strength, but, on the other hand, showed at later periods signs of disintegration in the form of a network of cracks on the outside. The fracture was very granular at all times, with no evidence of crystallization visible to the naked eye. The specimen containing 10 per cent of plaster and broken at the expiration of one year showed three distinct concentric zones. The outer one, about one-sixteenth of an inch thick, of a very friable nature, was mainly the carbonation product following the hydration. The next zone, of a thickness about equal to the outer one, was distinctly darker in color, fairly dense, and very tough, and was marked by the greatest amount of crystallized products, especially needles and hexagonal plates of hydrated tricalcium aluminate, a marked amount of gypsum, and a less amount of small needles of tricalcium sulphoaluminate ($3CaSO_4.3CaO.Al_2O_3 + H_2O$). The rest of the interior of the briquettes was again soft and was composed mainly of the amorphous hydrated tricalcium aluminate, though the crystallized variety of this compound was very evident; the amount of gypsum and sulphoaluminate in it was distinctly less than in the second tough zone.

2. DICALCIUM SILICATE

The dicalcium silicate is the compound which is always considered as giving the late strength to normal Portland cement, but just when it begins to hydrate sufficiently to impart more strength was

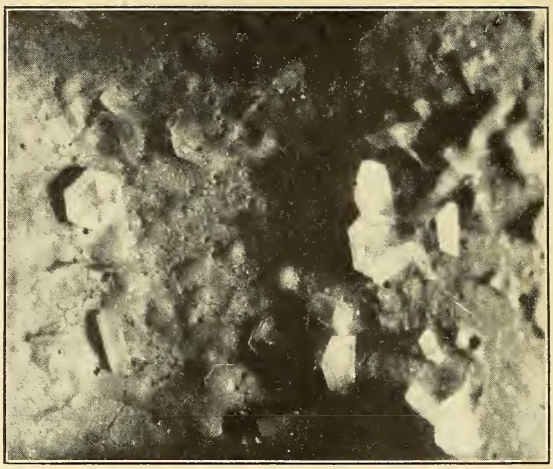

FIG. 10.—*The waist of a neat briquette of $2CaO.SiO_2$ stored in water away from contact with the air*

The water not having been renewed, soon became saturated with $Ca(OH)_2$, which later deposited on the briquette, and after nine months appeared as shown. These crystals are colorless, as is seen in several cases where the light has been normal to their surfaces; the more prominent ones are milky white, owing to air occlusion. Also note the crazing on the surface of the briquette. (×2.25.)

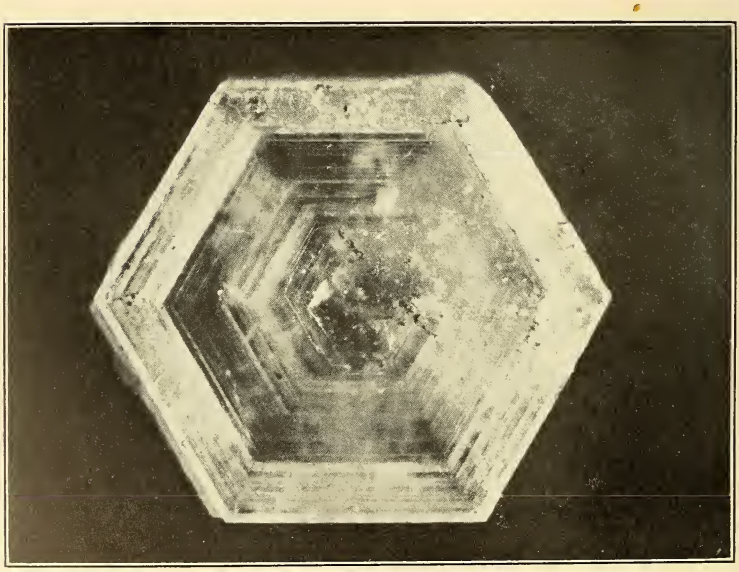

FIG. 11.—*The large $Ca(OH)_2$ crystal seen in the left center of figure 10, removed and photographed with a black background* (×20)

not known. Alone, even when containing as much readily hydrating material (alumina) as shown by the chemical analysis, it had so little strength at the period when Portland cement is usually tested that it is almost negligible, even though it is the major constituent. Almost one-third of the test pieces were lost on attempting to remove them from the molds at the end of 48 hours; at the end of 7 days they could be crushed readily in the hand; at the end of 2 weeks one test piece broke at 69 pounds and another at 53; no attempt was made to break any at 4 weeks, as apparently they had hardened but little since the 2-week period, but at the end of 13 weeks they had attained a strength of slightly over 500 pounds. They showed but little gain in strength between that period and 1 year. This is due to the character of the hydration, which is very slow and furthermore yields a product that is almost entirely amorphous, coating the exterior of the grains and preventing further access of water. The test pieces were very granular even at 1 year, with a marked lack of denseness, and do not possess a stone-like appearance; this structure allows the deposition of large crystals of lime hydrate. (See Figs. 5 and 10 to 17.) While Klein and Phillips [5] were not able to note the formation of these crystals in the hydration of the dicalcium silicate, they have since noted their formation on microscopic slides, when the amount of water present was very small compared with the amount of material; but when repeating their previous manipulation with relatively small amounts of dicalcium silicate and large amounts of water, the crystals again did not form. This former condition is fulfilled in the case of a test piece. These crystals are, however, not numerous, but are of a size to be easily noted by the naked eye after the six-month period.

The addition of either plaster or tricalcium aluminate to this compound causes a slight increase in strength at all periods. It was even possible to make 1:3 mortar specimens and to be able to remove them from the molds at a reasonably early period, though there was but little increase in denseness; but when plaster and the aluminate were added at the same time, the increase of denseness was quite evident, especially at the later periods. This was accompanied, however, by a decrease in strength (less than that shown when either of the two materials was used alone with the silicate) by the neat test pieces, but an increase was shown by the sand test pieces.

No satisfactory explanation is offered of this difference in relative strength of the neat and mortar test pieces, depending upon

[5] Tech. Paper No. 43, this Bureau.

whether the aluminate or plaster alone or these two together have been added to the dicalcium silicate. All the test pieces show consistent gain, but in the former case it has been much greater than in the latter, excepting the mortar test pieces, where the presence of the plaster and aluminate together has produced a greater gain. While the neat test pieces of the latter mixture show a greater denseness at the one-year period than any of the others, yet it is difficult to see, if an increase in this characteristic accompanies an increase in strength, why it should not affect both the neats and mortars in the same manner. While this increase in denseness may result in time in a setting up of strains, causing low strength, such can not be the case here, since the granular nature of the test pieces is still too pronounced (see Fig. 18) and also since the production of internal strains would hardly allow of increasing strengths such as shown.

3. TRICALCIUM SILICATE

The part of the tricalcium silicate in adding strength to normal Portland cement has not been studied, neither has its effect been a matter of much conjecture, as its presence has not been known definitely and differentiated from the tricalcium aluminate sufficiently long. As "alite" it has been assumed to give the early strengths, but "alite" includes, apparently, both the tricalcium aluminate and the tricalcium silicate, though all the optical data given by the various investigators using these terms are too indefinite to enable one to decide just what compounds are included under this name.

This compound alone had all the properties of Portland cement when gauged with water, either as a neat or a mortar test piece. The addition of plaster increased the early strengths somewhat, but did not affect the later ones; the aluminate when added to this compound, containing the oxide of chromium, caused a decided decrease in strength, but acted like plaster with the compound containing the boracic acid. (This is the only case when either the dicalcium or tricalcium silicate containing the chromium or boron oxide did not act similarly.) Plaster and the aluminate together also gave high early strengths. The addition of dicalcium silicate to the tricalcium silicate caused a decided decrease in early strength with a very good increase later. The addition of plaster and the aluminate, either alone or together, to the mixture of the two silicates increased the early strengths and, while still showing good gains at the last period, still they had not reached the limit developed by the silicate mixture alone.

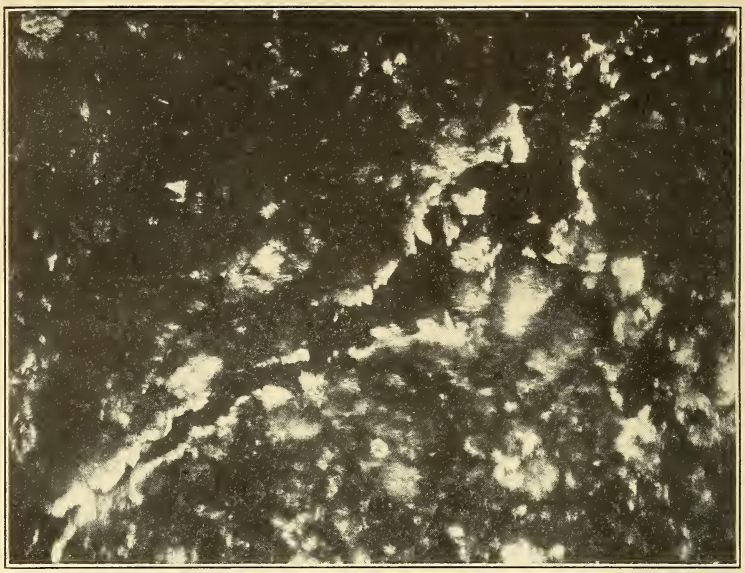

FIG. 12.—*A crack in the thin section of the one-year briquette of 3SSA, examined with crossed nicols*

The white material along the edge of the crack is $Ca(OH)_2$. (×165.)

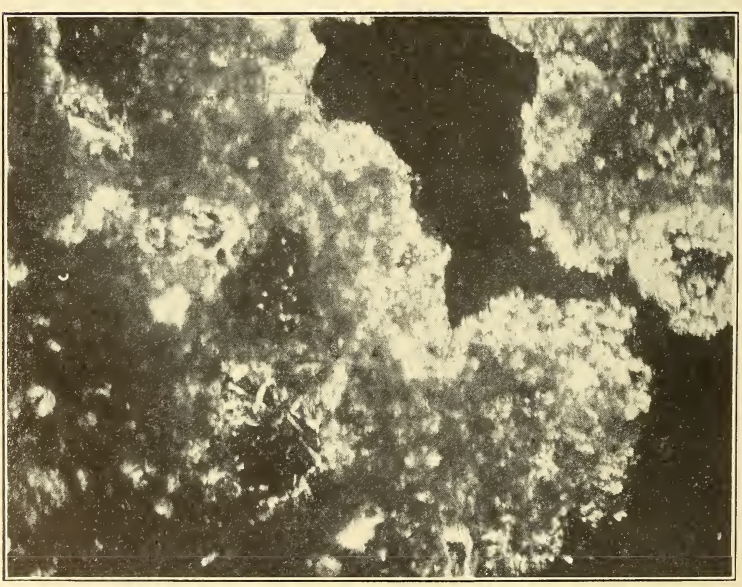

FIG. 13.—*A crack in the same thin section from which figure 12 was made, examined with crossed nicols*

The white material along the edge is $CaCO_3$. A number of rounded voids are seen to the left of the crack. These contain white imperfectly developed needles of $3CaO.Al_2O_3.XH_2O$ (hydrated tricalcium aluminate). (×165.)

The relative denseness of the test pieces at different periods was very interesting. (See Fig. 18–20.) The tricalcium silicate at 28 days was almost vitreous and glistening in appearance. The addition of any material but the plaster decidedly decreased this denseness, this being particularly marked at the early periods. While the denseness increased with age, yet the test pieces made of all mixtures, excepting the tricalcium silicate and plaster, did not break with the conchoidal smooth surface of the former, but either with a rough surface as when the dicalcium silicate was present or with a surface of a large number of smooth intersecting faces as when the aluminate was present. (See Fig. 20.)

4. BURNS 35 TO 39

The burns 35 to 39, as under time of set, again have a striking similarity to the mixtures which they approximate. The very low strengths of 35 and 38, which approximate the dicalcium silicate or its mixtures, are striking when the strengths of the latter are referred to. The addition of plaster to both of these burns, or aluminate to 35, has acted very much as the addition of these to the dicalcium silicate. The resemblance of 36 and 37 to the tricalcium silicate and its mixtures is just as striking.

Summarizing this discussion of the strengths of the individual compounds or their mixtures, it is quite evident that the dicalcium silicate adds but little to the strength of the mixture until after 28 days; that the tricalcium silicate has attained the greater part of its strength in 7 days; that the addition of plaster causes an increased early strength; and that the aluminate, without the presence of plaster, instead of adding strength decreases it.

VI. RATE OF HYDRATION

In order to correlate the strength developed by the various compounds with the rate of hydration, one of the test pieces for each period, after breaking and having had its surfaces quickly removed on an emery wheel, was crushed into small pieces and dried a little below 100° until it was sufficiently dry to allow of further grinding in a mortar without caking. The material, then ground until all passed a 100-mesh sieve, was dried at 102° until, after two hours heating, it would not show more than one-tenth of 1 per cent loss in weight. The ignition loss over a blast lamp and the amount of carbon dioxide were then determined on the sample thus prepared, the results being shown in Table 6 and Fig. 1, the ignition loss including the carbon dioxide.

47222°—17——3

These results are open to some criticism. The products of hydration are such that they lose water of hydration below the temperature at which they were dried. The gypsum resulting from the hydration of the plaster of Paris and the tricalcium sulphoaluminate resulting from the hydration of the aluminate and the plaster of Paris are of this nature, as is also possibly the hydrated tricalcium aluminate; the hydrated silicates, which are largely of a gelatinous or colloidal nature, also undoubtedly lose water slowly. But even under these adverse conditions the results undoubtedly show the relative amounts of hydration of the various compounds, and they also show very strikingly the difference in the rate of hydration of each and how this is affected by the presence of a second or third compound, as in the mixtures.

Taking first the question of the addition of plaster to any of the compounds or their mixtures, it is noted that this addition has produced but a slight change; further, it is noted that this slight change is most marked at the early periods. This agrees entirely with the strength results, where it was noted that the most marked effect of the addition of plaster was a slight increase at the early periods.

Next considering the individual compounds, the great difference which was shown between these in the rate and amount of development of strength is even as clearly shown in the rate and amount of hydration at different periods. The aluminate was so clearly unevenly hydrated that it was not deemed advisable to waste much time in determining the amount of water at the various periods, but such determinations as were made clearly show that the compound hydrates almost immediately and rather completely. This hydration, as is common with most compounds hydrating so quickly and with such a rise of temperature, did not result in the development of strength. The dicalcium silicate at the end of one year had less than 6 per cent of water of hydration, and had gained only about 1¼ per cent since the 13 weeks period. During this same length of time it had gained but little in strength. While no determination of the amount of hydration at 28 days was made, it was shown that it had gained nearly all of its strength between 28 days and 13 weeks. The tricalcium silicate between the 24-hour period and the 1-year period doubled the amount of hydration, but between the 28-day period and the 1-year period it gained only about 15 per cent; it had also gained all of its strength at 28 days—in fact, nearly all of it in 7 days.

The addition of the aluminate to the dicalcium silicate or mixtures of the two silicates produced apparently a very marked

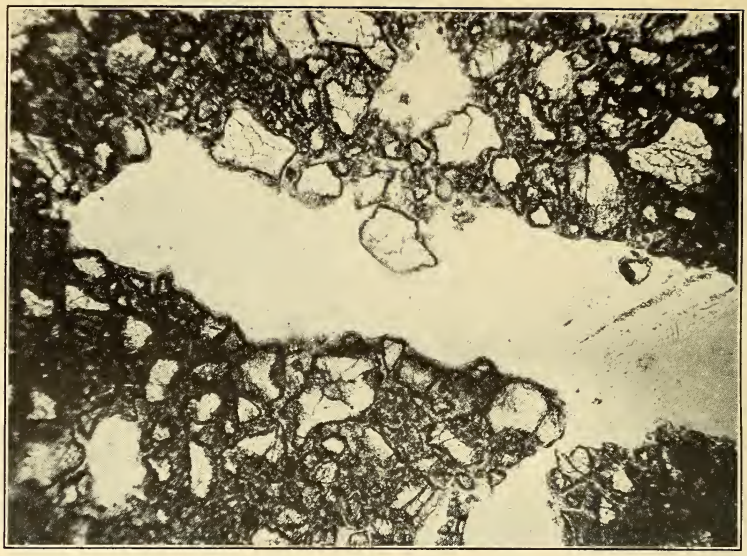

FIG. 14.—*A void in a thin section of the one-year briquette of* $2CaO.SiO_2$

The void, appearing white, apparently empty, extends almost entirely across the field. (×90.)

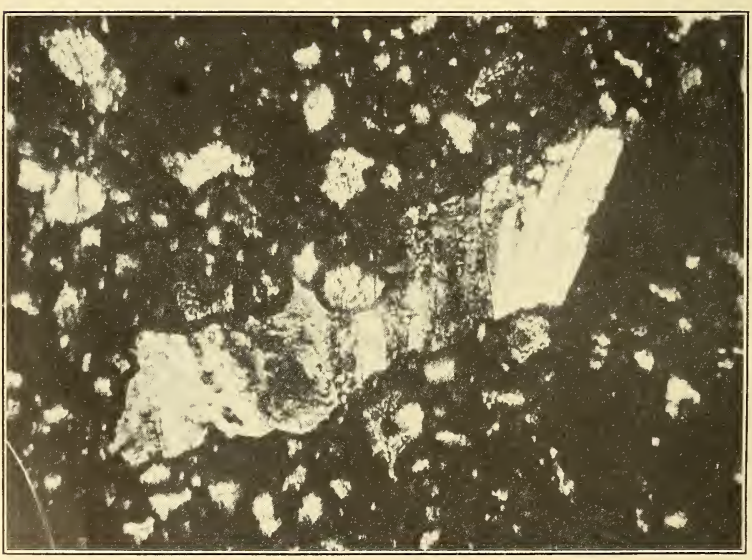

FIG. 15.—*The same as figure 14, but examined with crossed nicols*

Shows the void, all but one end, filled with $Ca(OH)_2$. It also shows more distinctly the difference between the hydrated (black) and unhydrated (white) silicate. Compare also with figure 5, where this is reproduced in its true color. (×90.)

increase in the amount of water of hydration in the mixture at all periods; but taking into consideration the amount of each compound present and its water of hydration as determined at any period, a simple calculation will show how much water of hydration should be present in any mixture at the same period. Such a calculation shows that the aluminate has not produced in any chemical or physical-chemical manner a very marked increase of hydration for that period in the silicates. Thus, 3SSA is composed of 40.5 per cent dicalcium silicate, the same amount of tricalcium silicate, and 19 per cent tricalcium aluminate; this mixture, made from the silicates containing the oxide of chromium, should have had 1.86, 4.53, and 3.68 per cent water, respectively, at 13 weeks for each of the compounds in it, or a total of 10.07 per cent. The determination made on the mixture at that period showed 10.97 per cent. A similar calculation for 3SA gives 12.75 and 13.83 per cent for the calculated and determined amounts, respectively; and for SA 7.38 and 8.62 per cent, respectively. At the later periods the aluminate has not increased the hydration any more, as can be readily seen on inspecting the values for the year period.

The mixture of the two silicates at any period seems to contain a little more water of hydration than it should have according to the calculation. It would appear, therefore, that one of the silicates had produced an increased hydration in the other, but this amount is very slight—but little more in amount than appeared, in the case of the addition of the aluminate to mixtures, between the calculated and determined values of the hydration.

When the results showing the rate of hydration of burns Nos. 35 to 39 are examined, it is noted that they follow very closely the purer compounds and the mixes made therefrom. Such might not appear to be the case, when the results of No. 35 at one year (9.56 per cent water) are compared with the results of S (5.50 per cent water) for the same period, and remembering that No. 35 contained only about 1.2 per cent alumina, being a dicalcium silicate raw mixture burned with a small amount of alumina as an impurity and mineralizer; but it should also be remembered that the result of this burning was not only the dicalcium silicate, but also some tricalcium silicate. Also No. 36, an impure tricalcium silicate raw mixture, contains some dicalcium silicate when burned, and consequently at the end of one year the water of hydration as determined was less than the tricalcium silicate 3S. The addition of plaster had the same effect on the burn as on the pure compound. The addition of more aluminate to 35 and 36 has not increased the rate of hydration of either.

The discussion of the results shown in Table 6, in connection with the results shown in Table 5, shows how the rate and amount of hydration follows the rate and amount of development of strength; but it is also seen in a large number of cases that, while the amount of hydration is increasing, the gain of strength has reached a maximum. This is especially noticeable in the case of the tricalcium silicate and the mixtures in which it forms the greater part. During its hydration a large amount of colloidal matter is formed which, with continued action of water, absorbs an increasing amount of water with a resulting increasing denseness of the test piece. This property of colloidal matter of absorbing very large amounts of water in a comparatively short time undoubtedly develops to a marked degree the strains in the test pieces produced by the original inability to make these uniform. In the case of the dicalcium silicate much less colloidal matter is produced by its hydration, and the long-time test pieces show marked granularity and openness of structure; the strength developed by this compound tend to show an increase in longer periods over those developed by the tricalcium silicate.

While the microscopical determination of the rate of hydration showed that at a very early period nearly all the tricalcium silicate had hydrated, yet it does not follow that this hydration is complete. Microscopically, the compound has hydrated when it has lost its optical identity but, part of the product of the hydration being colloidal, this latter may hydrate further (absorb more water) over very long periods. It may in fact absorb so much that it will lower its cementitious qualities, at the same time expanding very greatly in volume, as can be very readily shown by shaking up cement, either fresh or ground test pieces, with large volumes of water for various long periods. This latter was done with the year-test pieces of S (green) and 3S (green), about 12 grams of the ground material being shaken several times in the course of a day for one month with 200 cc of water. The water was then removed and after drying to constant weight at 102° C the former was found to contain 6.7 per cent water and the latter 14.5 per cent, as compared with approximately 5.3 per cent and 11.3 per cent in the test pieces. With this increase in hydration the apparent volume increased to five times its original value.

Hydrated Portland cement as a binder must be considered largely as an inorganic glue, and furthermore it has many of the properties of an organic glue; in other words, it is largely a reversible colloid. Fish or bone glue which has been used to cement two bodies (as two pieces of wood) together will, if placed

FIG. 16.—*A thin section of a one-year briquette of 3SS*

This is a void which shows a slight indication of the presence of transparent colorless crystals. (×165.)

FIG. 17.—*The same as figure 16 but examined with crossed nicols and showing the void almost filled with* $Ca(OH)_2$ *crystals* (×165)

in water, swell to such an extent that it will lose all its adhesive properties; if allowed to dry out, it will reach such a stage that it will again recover all its cementitious properties, and if further dried it will again lose this, being reduced to a very friable material. Portland cement acts in a somewhat similar manner, though ordinarily this can not be followed as readily, owing to the character of the materials cemented together. These are invariably very dense and do not allow the ready access of moisture to the cement. Also, the collodial matter formed from the cement does not allow so ready a passage of moisture; but the increased absorption of water can be readily followed by the increased denseness of neat test pieces, as noted when broken after various lengths of time (see Fig. 21), and the increasing loss of water can also be as readily followed by drying out long-time test pieces, in an atmosphere free from carbon dioxide, by the increase in dullness of luster and chalkiness in the hydrated material.

The results of the investigation would make it appear as if the presence of alumina was undesirable; thus, it has not improved the strength of either silicate, neither has it materially increased their amount of hydration, and it has tended to produce an unfavorable quick set. The presence of plaster has been necessary to offset partly these undesirable properties. Undoubtedly the question of the presence of alumina is one of a manufacturing necessity more than anything else. It is necessary as a flux in the burning of the clinker; without it the manufacture of cement, as it is now effected, would be a commercial impossibility. The tricalcium silicate with all its desirable properties is at the present not a manufacturing possibility from an economic standpoint. The dicalcium silicate, which could be manufactured, could not be used on account of its very slow set. Therefore, by adding alumina to a raw mix, the temperature of clinkering is reduced to economic commercial possibilities, and by decreasing the lime content to an amount approximately halfway between a dicalcium and a tricalcium silicate, a clinker is obtained which contains both the tricalcium and the dicalcium silicates, which are really necessary for both early and later strengths. Undoubtedly commercial Portland cement, when produced with very low alumina, gives very unsatisfactory results at early periods. In such cases the reactions have proceeded so far short of completion that great quantities of free lime are present, which necessarily gives poor cement. But the alumina must be considered a manufacturing necessity and only a means toward our end; in itself in the finished cement it is of a somewhat doubtful value.

VII. MICROSCOPIC DETERMINATION OF THE RATE OF HYDRATION

At the periods at which test pieces were broken microscopic examination was made of the broken pieces to determine the relative amount and kind of the hydration products. Also some thin sections of the test pieces, as well as polished surfaces of the same, were made and examined. This part of the investigation is of value more for the determination of the kind of the hydration products and the effect of one compound on another in the mixtures than for obtaining an exact idea of the relative amount of the hydration. When it is remembered that the dicalcium silicate showed by chemical analysis an increase of only 1.25 per cent water of hydration between 13 weeks and 1 year, the difficulties of comparing microscopically the hydrated products of the two periods can be appreciated. A description of the hydration compounds and of the optical constants of the crystalline hydration compounds has already been given by Klein and Phillips.[6]

No examination of the briquettes of S, SA, or SP was made before the 13-weeks period. At this period there was no difference distinguishable in the amount of hydration of the dicalcium silicate of either of these three and, further, by far the major portion of it was unhydrated. Crystals of lime hydrate were noted; the rest of the products of hydration were amorphous, except that there were present some of the crystalline variety of the hydrated aluminate, when this compound was present in the mixture, and gypsum crystals when plaster had been added. The only difference noted at the later periods was a slight increase in the amount of the crystalline variety of the hydrated aluminate.

When plaster as well as the aluminate had been added to the dicalcium silicate, the crystalline tricalcium sulphoaluminate was noted at the first period at which briquettes were examined—four weeks. The crystals were very minute and scattered through the amorphous products of hydration. The aluminate at this period was practically completely hydrated and the amount of the crystalline variety of the hydrated product was greater than when the plaster was not present in the mixture (SA). At the later periods the only changes noted were a comparatively slight increase in the amount of amorphous products of the hydration of the dicalcium silicate and an increase in the amount of crystalline variety of the hydration of the aluminate at the expense of the amorphous variety. Lime hydrate crystals were noted at all periods, not many in number, but large in size and well developed.

[6] Tech. Paper No. 43, this Bureau.

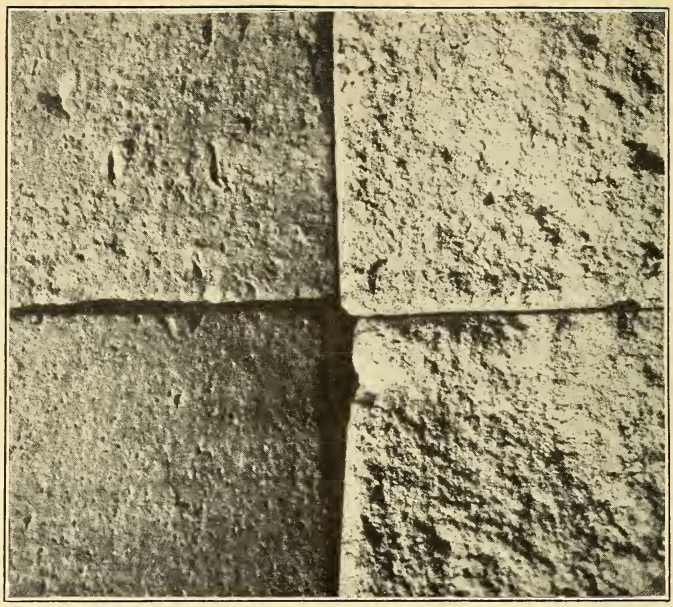

FIG. 18.—*Fractures as obtained in the testing machine of neat briquettes broken at various times*

Upper, right, one-day briquette of 3S; left, seven-day briquette of 3S. Lower, right, one-year briquette of S; left, one-year briquette of 3S. Note the increased denseness of the 3S briquette, also the rate at which this denseness has increased, at seven days being almost as dense as at one year; note also the year briquette of S, which compares favorably with 3S at one day for lack of denseness. (×3.)

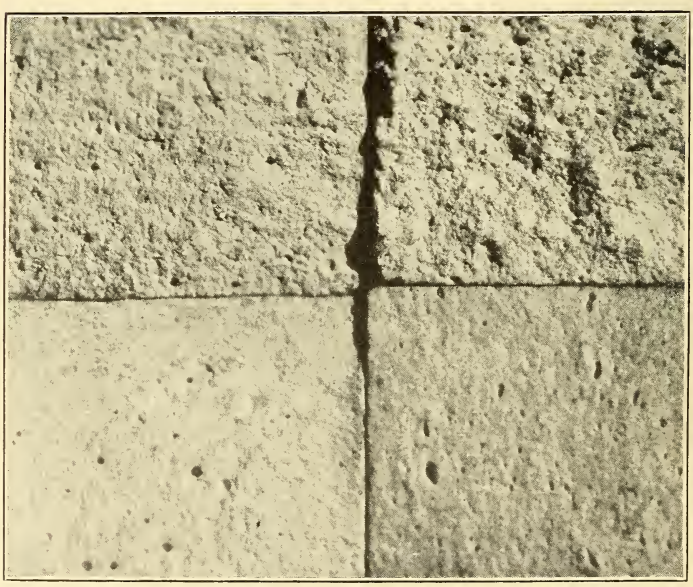

FIG. 19.—*Fractures obtained in breaking some of the briquettes of burns 35 and 36*

Upper, right, burn 36, one-day briquette; left, burn 35, one-day briquette. Lower, right, burn 36, six months; left, burn 35, six months. Note the increased denseness at the six months' period. (×3.)

The tricalcium aluminate seemed to hydrate a little more rapidly when increasing amounts of plaster were present, but even at 13 weeks with 10 per cent of plaster there was still some unhydrated aluminate. (Note, however, the difficulties mentioned previously in gauging this compound with water.) It could not be positively stated that the addition of the plaster caused an increased rate of the transformation of the amorphous variety of the compound to the crystalline, this transformation depending more upon the time factor. The aluminate test pieces at one year showed complete hydration, the product being largely of the amorphous variety; the crystalline variety existed as hexagonal needles and plates distributed through the mass (see Fig. 13); the sulphoaluminate needles occurred in the same manner but were very minute.

The tricalcium silicate showed at the end of 24 hours considerable hydration to an amorphous mass of hydrated silicate and minute crystals of lime hydrate. At the end of seven days the major part of the silicate was hydrated to the same products, while at the end of four weeks but little unhydrated compound remained. From this period on there was but little change; the silicate appeared always amorphous and the lime hydrate was distributed in very minute, poorly formed crystals through the mass. The latter compound did not show as good a development as when noted under conditions where its growth was unimpeded, e. g., when on surfaces of briquettes or on microscopical hydration slides. Its growth was hindered by the simultaneous rapid formation of amorphous hydrated silicate, and consequently it was noted either in very small individual crystals or in radialites. The former were for the most part allotriomorphic, i. e., they did not show their own crystal form. The radialites were small, round, and consisted of crystallites radiating from a common center. With plane polarized light and crossed nicols these never showed total extinction. Only those crystallites were in extinction whose optical directions were parallel to the vibration directions of the nicols, while the rest of the spherulite showed interference colors of the first or second order. In cavities within the briquettes the development of calcium hydroxide crystals was unrestrained, and fairly large, well-developed, hexagonal plates were noted.

The addition of plaster had produced a hardly noticeable increased hydration of the silicate at the end of 24 hours; after this period these test pieces could be distinguished from those not containing plaster only by the presence of minute gypsum crystals. The effect of the addition of tricalcium aluminate to

tricalcium silicate was similar to that produced by the addition of plaster to the compound; the aluminate in this mixture hydrated in the same manner as it did by itself, though it did go over to the crystalline variety more rapidly. The addition of both aluminate and plaster to this silicate produced no changes not already noted, except of course the appearance of the very minute sulpho-aluminate crystals scattered through the amorphous mass.

The mixture of dicalcium silicate and tricalcium silicate (3SS) hydrated as did the individual compounds; the former showed the first marked indication of hydration at four weeks and the latter showed almost complete hydration at the same period. The addition of aluminate or plaster, or both of these, to this silicate mixture did not produce any effect upon the products of hydration of either of the silicates, and in turn they were not very materially affected, with the possible exception of a greater development of the crystalline variety of the aluminate.

The examination of the hydrated burns (Nos. 35 to 39) showed the same general course of reaction as in the compounds—almost complete hydration of the aluminate at the end of 24 hours, a very rapid hydration of the tricalcium silicate almost completed in 28 days, and the very slow hydration of the dicalcium silicate—just starting at 28 days and very incomplete at the end of 1 year. The lime hydrate appeared in much larger crystals in those test pieces that were high in ortho-silicate, largely because these are very granular, with plenty of fair-sized voids in which they can grow unrestrained; whereas very dense test pieces, high in tricalcium silicate, allowed these crystals to grow more rapidly on account of the greater amount of lime freed by hydration, but caused them to form in a very minute form scattered through the mass of the amorphous hydrated silicate. The addition of plaster to these burns increased the hydration of the dicalcium silicate to a slight extent, this being particularly noticeable at the 28-day periods; other than the appearance of sulphoaluminate and gypsum crystals, no other differences were noted. The addition of aluminate to burns 35 and 36 produced no marked change in the former, but in the latter there was apparently a much greater increase in the amount of tricalcium silicate hydrated at 7 days than when this compound was not present.

Following the progress of the hydration by the microscope shows, therefore, that the dicalcium silicate does not start hydrating to any marked extent before 28 days, and that it then forms an amorphous hydrated silicate and crystalline lime hydrate.

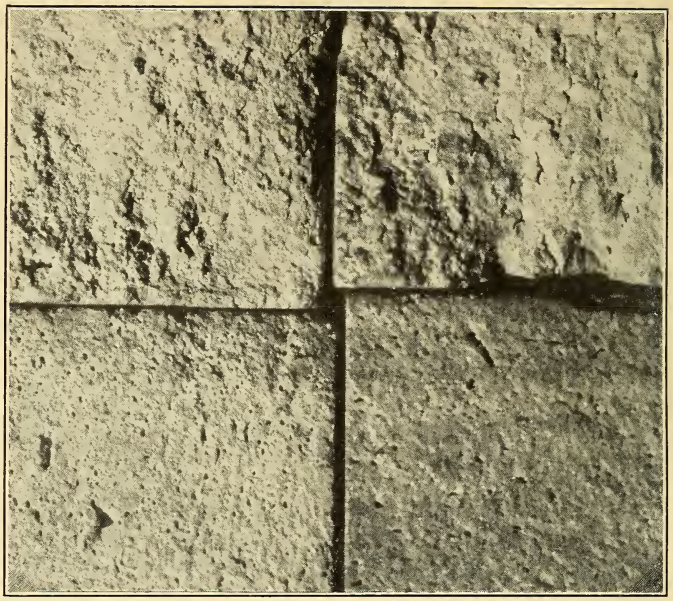

FIG. 20.—*Fractures obtained in breaking in the testing machine various briquettes of S and 3SA*

Upper, right, 3SA broken at one year; left, 3SA broken at seven days. Lower, right, 3S broken at one year; left, 3S broken at seven days. Note the lack of evenness of the fracture which the aluminate produced in the briquette, and also the large number of short, rather wide cracks. These usually contained crystalized $Ca(OH)_2$. (See Fig. 12.) (×3.)

FIG. 21.—*Fractures obtained in breaking at different periods neat briquettes of a commercial Portland cement*

Upper, right, broken at one day; left, broken at seven days. Lower, right, broken at one year; left, broken at four weeks. The rate of decrease of sandiness with increase of age is very noticeable. (×3.)

The latter in time grows to large crystals (Figs. 10, 11, 14, and 15), owing to the very slow liberation of the lime and because the lack of denseness of the test pieces provides voids in which it can grow unrestrained. The tricalcium silicate hydrates almost completely in 28 days to an amorphous hydrated silicate and minute crystals and radialites of lime hydrate scattered through the mass of amorphous material. The formation of the fine crystals in place of large crystals, such as form in the dicalcium silicate, is due to the fact that the conditions accompanying their liberation and formation are just the opposite of those obtaining in the case of the dicalcium silicate. The tricalcium aluminate hydrates very rapidly to amorphous tricalcium aluminate without any liberation of lime. After a short time the crystalline variety is formed at the expense of the amorphous. When this compound is mixed with other materials the rate of hydration and change to the crystalline variety is more rapid than when masses of it alone are gauged with water, owing to these preventing its agglomerating into masses, the interior of which hydrates very slowly. Mixtures of the silicates alone, or with the aluminate, or with plaster, or with plaster and the aluminate, differ but little from the hydration of the compounds alone, though apparently the tricalcium silicate reacts a very little more rapidly in the presence of the aluminate or plaster. When aluminate and plaster are present, very minute needle crystals of tricalcium sulphoaluminate are produced, in addition to gypsum crystals, which always appear when plaster is present.

VIII. CONCLUSIONS

1. At early periods the constituents of Portland cement of normal composition and manufacture, in the order of their strength-conferring properties, are: Tricalcium silicate, tricalcium aluminate, and dicalcium silicate.

2. At periods beyond 28 days the dicalcium silicate gains sufficient strength to place it almost on an equality with the tricalcium silicate.

3. Tricalcium aluminate containing 10 per cent plaster gains practically no strength after the first period at which it was tested; that is, 24 hours.

4. Tricalcium silicate of the purity used in this investigation (90 per cent 3 $CaO.SiO_2$ in one case and 95 per cent in the other) has all the important properties of Portland cement, especially those of the "rate of setting" and strength developed.

5. Dicalcium silicate, such as used in this investigation, sets too slowly and attains strength too slowly to be of any commercial value when used alone.

6. Tricalcium aluminate alone, as used in this investigation, sets too rapidly and attains too little strength to be of any commercial value as a hydraulic cementing material.

7. Tricalcium aluminate, when used to replace about 19 per cent of the dicalcium silicate (which is approximately the amount of aluminate present in Portland cement) adds somewhat to the strength of the latter at the later periods. This mixture when used with the addition of 3 per cent of plaster gives lower strengths than the silicate alone, as neat test pieces, but as a 1:3 mortar the strengths are higher than any of the dicalcium silicate mixtures not containing the tricalcium silicate.

8. Tricalcium aluminate, when used to replace about 19 per cent of tricalcium silicate, did not add to the strength of the latter, showing rather a slight tendency to decrease it. The addition of 3 per cent of plaster gave higher early strengths but lower later ones.

9. Tricalcium aluminate, when used to replace about 19 per cent of a mixture of equal parts dicalcium and tricalcium silicate, increased the strength at 24 hours and 7 days, but decreased it at the later periods. The addition of 3 per cent of plaster increased the strength at all periods

10. Plaster of Paris, when added to any of the compounds or mixtures of those studied, generally increased their strength. This effect is more marked at the early periods.

11. The amount of water of hydration of any of the compounds at any period is not a measure of the strength developed, as the dicalcium silicate at one year with 5.5 per cent water of hydration has a strength almost as great as the tricalcium silicate with 11.5 per cent, whereas the tricalcium aluminate with 26.4 per cent has a strength of less than 100 pounds per square inch.

12. The dicalcium silicate hydrates to a very granular porous mass which allows of ready egress of solutions and, while it is chemically more resistant to the action of solutions than the tricalcium silicate, yet it furnishes a great number of voids in which salts may crystallize out of solution, and it is consequently very little able to resist the mechanical action of the "freezing out" (crystallization) of salts from solution.

13. On the other hand, the hydrated tricalcium silicate with its very dense structure, composed of gelatinous (colloidal) silicate

interspersed with crystals of lime hydrate, is probably very susceptible to strains produced by alternate wettings and dryings, colloidal material of this kind being subject to considerable volume change resulting from slight moisture changes.

14. It appears, therefore, that the composition of Portland cement should be along lines which would not produce a great preponderance of either silicate. The ideal cement should possibly have an excess of the dicalcium silicate, which would give a not too dense hydrated material, gaining strength at later periods. A lesser amount of the tricalcium silicate would furnish the desired early strength and also overcome the excessive porosity of the dicalcium silicate.

15. It is possible to make a cement that will have the properties of Portland cement by grinding together the previously separately burned constituents in approximately the amounts in which they exist in Portland cement.

16. The function of tricalcium aluminate in the finished cement is somewhat problematical. A cement with less than 1 per cent of alumina has all the properties of Portland cement. Such a cement is, however, not a commercial possibility from the manufacturing standpoint, on account of the temperatures and amount of burning involved. To state, however, that the aluminate in the finished cement is of the nature of a diluent or inert material would be drawing a conclusion which, while justified by the present investigation, requires further confirmatory work.

17. The actual products of the hydration are those noted by Klein and Phillips,[7] excepting as noted before the case of the dicalcium silicate, when apparently during the hydration of this compound lime hydrate is formed.

In carrying out the work in connection with this paper the authors have had the assistance of A. C. Nothstine and J. C. Evans in making the chemical analyses, and E. R. Gates in making and superintending the making of the physical specimens.

WASHINGTON, February 26, 1916.

[7] Tech. Paper No. 43, this Bureau.

TABLE 1

Microscopical Examination of the Compounds and Burns 35 to 39[a]

$2CaO.SiO_2$: Both of the dicalcium silicates show an irregular granular structure, with almost complete lack of true prismatic development; largest grains are 0.3 mm in diameter. The silicate containing the oxide of chromium shows a slight raising of the indices of refraction, being 1,719±003. The small amount of alumina present exists as $5CaO.3Al_2O_3$. The silicate is present in the beta form. (See Figs. 2 and 6.)

$3CaO.SiO_2$: The silicate containing boracic acid showed 90 per cent $3CaO.SiO_2$, 8 per cent $\beta 2CaO.SiO_2$, and 2 per cent CaO. The silicate containing chromium oxide showed 95 per cent $3CaO.SiO_2$, 4 per cent $\beta 2CaO.SiO_2$, and 1 per cent CaO. Both are extremely fine grained, with very slight indications of crystalline development.

$3CaO.Al_2O_3$: Entire lack of crystalline outline; consists almost entirely of $3CaO.Al_2O_3$; a very slight amount of $5CaO.3Al_2O_3$; and traces of $2CaO.SiO_2$ and CaO.

Burn 35: Very regular large-grained $\beta 2CaO.SiO_2$; markedly different from the irregular-grained pure $\beta 2CaO.SiO_2$ above. The aluminate occurs as a flux between the grains. No $3CaO.SiO_2$. (See Figs. 3 and 7.)

Burn 36: The alumina has increased very decidedly the size of the grains of the $3CaO.SiO_2$ over that obtained in the pure $3CaO.SiO_2$ above, and is present as $3CaO.Al_2O_3$ in very fine grains. About 5 per cent $\beta 2CaO.SiO_2$; remainder is $3CaO.SiO_2$. (See Fig. 9.)

Burn 37: A trace of $\beta 2CaO.SiO_2$; $3CaO.SiO_2$ is even more crystalline than in 36; $3CaO.Al_2O_3$ in minute grains, but largely as a flux between grains of the silicate.

Burn 38: Very largely $\beta 2CaO.SiO_2$, but grains are smaller than 35. Some $3CaO.SiO_2$, but segregated in large grains; $3CaO.Al_2O_3$ present in rather large amount between grains of $\beta 2CaO.SiO_2$. (See Figs. 4 and 8.)

Burn 39: Contains about 25 per cent $\beta 2CaO.SiO_2$; remainder is $3CaO.SiO_2$ and $3CaO.Al_2O_3$. Very little crystalline development; grain size of both silicates very small; $3CaO.Al_2O_3$ occurs as flux between silicate grains and in some cases in fair-size isolated grains.

TABLE 2

Proportion in Which the Burns Were Mixed and Reference Marks Used Hereafter

Reference mark	Mineralizer	Proportion: Parts by weight			Added, $CaSO_4.5H_2O$	Composition[b]							
		$3CaO.SiO$	$2CaO.SiO_2$	$3CaO.Al_2O_3$		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	B_2O_3	Cr_2O_3
S, white	B_2O_3		100			33.76	0.33	0.34	63.44	1.51		0.75	
S, green	Cr_2O_3		100			34.01	.21	.15	63.87	1.11			0.51
SP, white	B_2O_3		100		3	32.74	.32	.33	62.64	1.46	1.60	.73	
SP, green	Cr_2O_3		100		3	33.06	.20	.15	63.22	1.08	1.60		.50
SA, white	B_2O_3		81	19		27.49	7.32	.33	62.88	1.37		.61	
SA, green	Cr_2O_3		81	19		27.73	7.34	.17	63.30	1.05			.41
SAP, white	B_2O_3		81	19	3	26.69	7.11	.32	62.18	1.33	1.60	.59	
SAP, green	Cr_2O_3		81	19	3	26.92	7.13	.17	62.58	1.02	1.60		.40
A				100		.67	37.67	.27	60.32	.79			
3A				100	3	.65	36.67	.26	59.85	.77	1.61		
10A				100	10	.61	34.36	.25	58.54	.72	4.95		
3S, white	B_2O_3	100				26.21	.20	.49	70.53	1.11		.96	

3S, green	Cr_2O_3	100				25.34	.23	.40	71.22	1.55			.62
3SP, white	B_2O_3	100			3	25.57	.20	.48	69.94	1.08	1.60	.94	
3SP, green	Cr_2O_3	100			3	25.46	.23	.39	70.71	1.51	1.61		.61
3SA, white	B_2O_3	81		19		21.46	7.35	.45	68.90	1.06		.78	
3SA, green	Cr_2O_3	81		19		20.77	7.38	.38	69.55	1.42			.50
3SAP, white	B_2O_3	81		19	3	20.83	7.14	.44	68 01	1 02	1.61	.76	
3SAP, green	Cr_2O_3	81		19	3	20.16	7.16	.37	68.64	1.38	1.61		.49
3SS, white	B_2O_3	50	50			29.98	.26	.42	66.98	1.30		.85	
3SS, green	Cr_2O_3	50	50			29.68	.22	.28	67.54	1.33			.57
3SSP, white	B_2O_3	50	50		3	29.16	.26	.41	66.27	1.27	1.60	.84	
3SSP, green	Cr_2O_3	50	50		3	28.91	.22	.28	66.95	1.30	1.60		.55
3SSA, white	B_2O_3	40.5	40.5	19		24.47	7.39	.39	65.85	1.21		.69	
3SSA, green	Cr_2O_3	40.5	40.5	19		24.25	7.37	.27	66.42	1.23			.46
3SSAP, white	B_2O_3	40.5	40.5	19	3	23.75	7.17	.38	65 06	1.18	1.60	.67	
3SSAP, green	Cr_2O_3	40.5	40.5	19	3	23.54	7.15	.26	65.60	1.20	1.61		.45

[a] For complete optical data for all compounds in the system $CaO.Al_2O_3.SiO_2$, see "The ternary system $CaO.Al_2O_3.SiO_2$," by Rankin; Am. Jour. of Sci., January, 1915; fourth series, Vol. XXXIV, No. 229.

[b] Composition calculated from analyses given in Table 3.

TABLE 3

Chemical Analysis of the Burns

	Mineralizer	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	B_2O_3	Cr_2O_3
$2CaO.SiO_2$	B_2O_3	33.76	0.33	0.34	63.44	1.51	0.75	
$2CaO.SiO_2$	Cr_2O_3	34.01	.21	.15	63.87	1.11		0.51
$3CaO.SiO_2$	B_2O_3	26.21	.20	.49	70.53	1.11	.96	
$3CaO.SiO_2$	Cr_2O_3	25.34	.23	.40	71.22	1.55		.62
$3CaO.Al_2O_3$		.67	37.67	.27	60.52	.79		
Burn 35	B_2O_3	34.44	.81	.13	62.94	1.40	(a)	
Burn 36	B_2O_3	25.93	1.27	.17	69.01	2.35	(a)	
Burn 37		21.82	7.42	.10	68.09	2.20		
Burn 38		28.50	7.46	.22	60.47	2.22		
Burn 39		25.30	7.34	.08	64.47	2.15		

[a] Not determined.

TABLE 4

Time of Set, Consistency, and Soundness

Compound	Color	Per cent H_2O used	Time of set (Gilmore)		Soundness [a]	Remarks
			Initial	Final		
			h. m.	h. m.		
S	White	19.5	1 00	5 00	O. K.[b]	No evolution of heat on mixing with H_2O. Gauged mass lacks plasticity.
S	Green	20.0	20 00	5 00	O. K.	Do.
SP	White	19.0	20 00	5 00	O. K.	No evolution of heat on mixing with H_2O. Somewhat more plastic than S.
SP	Green	19.0	28 00	5 00	O. K.	Do.
SA	White	20.0	[c] 3 15	24 00	O. K.	Much evolution of heat on mixing with H_2O. Marked increase in plasticity.
CSA	Green	20.5	[c] 7 00	24 00	Disintegrated	Do.
SAP	White	23.5	10	40	O. K.[b]	Less heat than in SA test pieces. More plastic than any of above.
SAP	Green	23.5	10	40	O. K.	
A [d]						
3A [d]						
10A [e]						
3S	White	22.5	2 05	4 20	O. K.	No evolution of heat. The gauged tricalcium-silicate is much more plastic than the dicalcium-silicate.
3S	Green	22.0	2 15	4 00	O. K.	Do.
3SP	White	22.0	1 05	5 10	O. K.	No evolution of heat. Slight increase of plasticity over 3S.
3SP	Green	22.0	35	5 05	O. K.	Do.
3SA	White	25.5	05	2 40	O. K.	Considerable evolution of heat. Very plastic.
3SA	Green	26.5	08	2 10	O. K.	Do.
3SAP	White	26.0	50	2 00	O. K.	Plaster did not reduce the evolution of heat. Most plastic of all.
3SAP	Green	26.5	35	1 40	O. K.	Do.
3SS	White	21.5	4 15	7 00	O. K.	No evolution of heat. Addition of S to 3S reduces plasticity markedly.
3SS	Green	22.0	3 10	5 05	O. K.	Do.
3SSP	White	21.0	1 50	6 00	O. K.	No evolution of heat. Addition of plaster to 3SS slightly increases plasticity.
3SSP	Green	22.0	1 05	5 05	O. K.	Do.

3SSA	White	24.0	15	3 20	O. K.[b]	Much evolution of heat. Addition of A to 3SS makes as plastic mass as 3SSP.
3SSA	Green	24.0	Flash.	2 20	O. K.[b]	Do.
3SSAP	White	25.0	1 05	1 35	O. K.	Less evolution of heat than 3SSA. About as plastic as 3SA.
3SSAP	Green	25.0	35	1 55	O. K.	Do.
35		22.0	6 00	22 00	O. K.	No evolution of heat. Nonplastic.
35P		21.0	1 05	5 30	O. K.	No evolution of heat. A little more plastic than 35.
35AP		25.0	1 55	3 20	O. K.	Marked evolution of heat. Marked increase in plasticity over 35 and 35P.
36		21.0	4 25	7 30	O. K.	No evolution of heat. Not very plastic but more so than 35.
36P		21.0	25	4 50	O. K.	No evolution of heat. A little more plastic than 35P.
36AP		24.5	1 55	2 35	O. K.	Marked evolution of heat. Good plasticity.
37		27.0	20	4 45	O. K.	Considerable evolution of heat. Good plasticity.
37P		25.0	2 00	4 35	O. K.	Plaster prevented high evolution of heat. Good plasticity.
38		19.0	10	2 00	O. K.	No evolution of heat. Nonplastic.
38P		17.0	25	1 20	O. K.	Do.
39		24.0	12	5 30		No evolution of heat. Good plasticity.
39P		22.0	3 45	6 00	O. K.	Do.

[a] In atmosphere of steam for four hours.

[b] Pats showed no signs of disintegration but lacked "ring" on striking.

[c] Not the proper initial set; these gave rise to great evolution of heat, which really gave a flash set; a trial of SA white, mixed rapidly with H_2O and pat formed quickly, gave an initial set of 22 minutes. (See text also.)

[d] Immediate hydration with all percentages of H_2O up to 72; accompanied by sufficient evolution of heat to make mass boil.

[e] No time of set, but carbonating of surface after several days.

TABLE 5

Tensile Strength of Neat and 1:3 Ottawa Sand Mortars

Compound	Color	Pounds per square inch. Tested at end of—						Remarks
		24 hours	7 days	28 days	13 weeks	26 weeks	1 year	
S neat	Green	Soft	Soft	(a)	513	621	.....	All test pieces show crystals of lime hydrate at end of 1 year distinctly visible to the naked eye. All test pieces show about the same degree of denseness at all periods, excepting SAP at 26 weeks, which is appreciably more dense than the others; SAP at 1 year was most dense of all and also showed an increase of this characteristic over the same test pieces broken at earlier periods. SA at 1 year was also distinctly more dense than at previous periods, but not as much so as SAP at 1 year.
					564	542	638	
S neat	White	Soft	Soft	(a)	493	.....	.....	
					507	.....	538	
SP neat	Green	Soft	Soft	133	643	633	795	
				135	616	685	740	
SP sand	do	Soft	Soft	b 22	122	238	196	
					135	.....	228	
SP neat	White	Soft	Soft	106	548	672	743	
				90	528	560	692	
SP sand	do	Soft	Soft	b 23	131	194	225	
					128	.....	195	
SA neat	Green	Soft	Soft	128	572	586	711	
				143	535	778	971	
SA sand	do	Soft	Soft	b 28	144	.....	140	
							183	
SA neat	White	Soft	Soft	152	588	627	812	
				170	492	783	938	
SA sand	do	Soft	Soft	b 21	160	.....	228	
							160	
SAP neat	Green	60	30	135	302	588	530	
		66	47	117	325	605	561	
SAP sand	do	.....	60	40	.....	235	346	
			67	52	.....	.....	.....	
SAP neat	White	95	109	178	385	389	668	
		100	102	206	368	370	561	
SAP sand	do	.....	44	54	.....	260	387	
			35	63	.....	.....	.....	

A neat [c]							162	A, 3A, and 10A very light sandy test pieces at all periods.
							124	
3A neat [c]								
		48	129	118				
10A neat		153	141	131			[d] 92	
3S neat	Green	258	653	716	730	765	702	
		217	634	835	729	700	602	
3S sand	do		190	328	310			
			160	283	338			
3S neat	White	240	545	755	730	666	672	
		208	441	959	800	674	695	
3S sand	do		182	305		472		
			200	341		462		
3SP neat	Green	323	582	730	750	670	540	Being more dense than the dicalcium silicate test pieces, these do not show crystals except under the microscope. The addition of S or A to 3S caused a marked decrease of denseness at all periods; the addition of P did not materially affect these results. At late periods the increase of denseness is very noticeable in all except 3S and 3SP, which have been very dense at all periods but 24 hours, these latter at later periods being almost vitreous and breaking with a conchoidal fracture.
		360	710	845	562	547	652	
3SA sand	do		242	358	365			
			220	358	371			
3SP neat	White	457	727	770	725	675	640	
		424	668	775	641	639	645	
3SP sand	do		267	393		385		
			274	420		358		
3SA neat	Green	248	392	225	440	275	468	
		261	483	281		300	560	
3SA sand	do		226	291	294			
			252	279	265			
3SA neat	White	254	731	713	600	785	715	
		287	653	525	740	635	680	
3SA sand	do		362	392		413		
			367	413		427		
3SAP neat	Green	439	863	587	530	472	743	
		391	757	552	585	415		

[a] No test pieces broken at 28 days; 1 white gave 69 and 1 green gave 53 at 14 days.
[b] Could be easily crumbled in the hand.
[c] Never hardened in water. Results given were obtained from test pieces stored in air.
[d] Briquette covered with network of cracks; not much enlarged, however.

TABLE 5—Continued

Compound	Color	Pounds per square inch. Tested at end of—						Remarks
		24 hours	7 days	28 days	13 weeks	26 weeks	1 year	
3SAP sand	do		279	311	336			
			276	300	339			
3SAP neat	White	259	732	905	525	546	553	
		275	595	912	600	556	693	
3SAP sand	do		313	420		351		
			347	370		361		
3SS neat	Green	68	246	589	852	819	891	
		105	250	540	720	865	720	
3SS sand	do		65	190	330			
			71	178	252			
3SS neat	White	77	277	612	717	722	785	
		102	266	615	644	638	732	
3SS sand	do		110	182		337		Being more dense than the dicalcium silicate test pieces, these do not show crystals except under the microscope. The addition of S or A to 3S caused a marked decrease of denseness at all periods; the addition of P did not materially affect these results. At late periods the increase of denseness is very noticeable in all except 3S and 3SP, which have been very dense at all periods but 24 hours, these latter at later periods being almost vitreous and breaking with a conchoidal fracture.
			101	155		292		
3SSP neat	Green	161	383	584	645	850	673	
		150	340	626	805	820	698	
3SSP sand	do		84	223	315			
			97	193	263			
3SSP neat	White	161	384	621	636	588	763	
		173	340	432	703	565	794	
3SSP sand	do		119	207		293		
			118	232		346		
3SSA neat	Green	135	326	332	422	496	626	
		132	345	345	380	459	615	
3SSA sand	do		60	130	195			
			60	140	111			
3SSA neat	White	174	438	437	490	453	580	
		175	532	432	420	506	586	

3SSA sand	do		212	262		480		
			201	235		443		
3SSAP neat	Green	255	470	610	663	719	630	
		295	321	685	574	743	751	
3SSAP sand	do		178	216	316			
			187	218	295			
3SSAP neat	White	333	365	697	670	685	875	
		281	498	646	692	656	751	
3SSAP sand	do		200	256		356		
			195	239		315		
35 neat		47	165	408	600	620	693	Crystals of $Ca(OH)_2$ distinctly noticeable at the end of 26 weeks. The addition of both A and P to 35 and 36 caused an increase in granularity at all periods; this was especially noticeable in the first three periods; later there was not so much difference in the denseness; 35 was more granular than 36 at all periods, the latter comparing favorably with 37 and 39.
		52	160	406	635	734	682	
35 sand			44	172		346		
			40	192		335		
35P neat		68	230	460	556	828	705	
		76	223	490	738	670	834	
35P sand			55	238		321		
			62	168		394		
35AP neat		163	239	305	543	678	760	
		152	218	294	403	725	662	
35AP sand			140	236		487		
			131	216		490		
36 neat		80	290	690	738	884	762	
		82	355	690	625	722	800	
36 sand			70	183		352		
			72	160				
36P neat		108	296	783	720	516	745	
		110	377	693	686	674	877	
36P sand			15	213		300		
			91	220		306		
36AP neat		332	724	830	950	900	900	
		246	700	817	810	916	978	
36AP sand			266	327		300		
			296	298		330		

TABLE 5—Continued.

Compound	Color	Pounds per square inch. Tested at end of—						Remarks
		24 hours	7 days	28 days	13 weeks	26 weeks	1 year	
37 neat		321	595	636	535	470	.....	No crystals except under the microscope. P has caused quite an increase in denseness; those containing P are very dense at 7 days; those without it are distinctly granular at 13 weeks.
		330	.....	590	.....	561	.....	
37 sand		.....	384	368	.....	405	.....	
			396	378	.....	414	.....	
37P neat		424	659	995	1045	930	952	
		437	593	1000	1157	838	975	
37P sand		.....	312	380	.....	430	.....	
			228	402	.....	416	.....	
38 neat		178	150	225	402	516	670	Many crystals of $Ca(OH)_2$ at 1 year. Very granular compared with 37 and 39. Addition of P has produced no effect on denseness; test pieces still quite granular at 90 days.
		162	163	127	455	682	486	
38 sand		.....	73	117	.....	410	.....	
			70	143	.....	360	.....	
38P neat		302	308	396	406	450	530	
		304	326	475	433	415	505	
38P sand		.....	83	208	.....	364	.....	
			83	206	.....	424	.....	
39 neat		177	402	800	800	657	572	No crystals except under the microscope. Addition of P has increased the denseness. All test pieces very dense at end of 7 days.
		246	532	582	725	537	617	
39 sand		.....	175	355	.....	430	.....	
			208	320	.....	316	.....	
39P neat		324	824	845	928	748	815	
		332	827	795	982	848	.....	
39P sand		.....	371	405	.....	447	.....	
			375	412	.....	492	.....	

TABLE 6

Amount and Rate of Hydration

Compound	Color	24 hours		7 days		28 days		13 weeks		26 weeks		1 year	
		CO_2	Ig. loss	CO_2	Ig. loss	CO_2	Ig. loss	CO_2	Ig. loss	CO_2	Ig. loss	CO_2	Ig. loss
S	White							0.28	4.25			0.54	5.50
S	Green							.31	4.58	0.35	5.11	.52	5.27
SP	White							.30	4.46		5.11	.40	5.60
SP	Green							.33	4.76	.39	5.11	.47	5.77
SA	White							.27	8.07	.33	8.80	.47	10.18
SA	Green							.28	8.62	.31	9.66	.50	10.26
SAP	White					0.26	6.37	.26	7.95		9.41	.59	9.80
SAP	Green					.25	6.55	.35	8.86	.37	9.26	.64	11.22
A								.17	19.42				
10A		[a] 0.28	[a] 19.40	0.98	24.00	.58	23.38					.70	26.43
3S	White	.46	5.53	.37	8.44	.59	9.62	.40	10.50	.56	10.70	.46	11.59
3S	Green	.45	7.40	.68	8.86	.41	10.80	.37	11.21	.31	11.31	.30	11.51
3SP	White	.44	8.63	.56	9.97	.67	11.00	.38	11.16	.59	11.62	.40	11.81
3SP	Green	.65	8.30	.56	10.34	.41	11.00	.37	12.20	.84	12.28	.31	12.76
3SA	White	.68	9.51	.45	10.76	.49	11.73	.65	12.20	.44	12.73	.62	13.76
3SA	Green	.58	10.91			.43	12.27	.30	13.83	.36	14.36	.34	14.58
3SAP	White	.56	10.33	.52	10.71	.43	12.14	.55	12.29	.34	12.67	.34	14.24
3SAP	Green	.81	11.02	.60	11.22	.31	12.49	.26	13.37	.42	13.04	.51	14.88
3SS	White	.34	3.50	.37	5.05	.41	6.96	.98	8.34	.87	8.65	.56	9.90
3SS	Green			.42	5.30	.35	7.40	.65	8.57	.25	9.24	.62	9.93
3SSP	White	.37	4.48	.44	6.20	.37	7.40	.60	8.29	.92	9.50	.42	9.60
3SSP	Green			.30	5.89	.40	7.78	.45	8.71	.44	9.22	.36	9.96
3SSA	White	.40	7.77	.46	9.35	.34	10.18	.41	10.97	1.29	11.43	1.29	11.71
3SSA	Green	.29	8.06	.35	9.48	.47	10.76	.28	10.97	1.32	11.93	1.49	13.07
3SSAP	White	.39	8.31	.40	10.44	.37	10.33	.47	11.70	.18	12.60	.29	13.24

[a] Determination made on test piece broken at end of 48 hours.

TABLE 6—Continued

Compound	Color	24 hours		7 days		28 days		13 weeks		26 weeks		1 year	
		CO_2	Ig. loss	CO_2	Ig. loss	CO_2	Ig. loss	CO_2	Ig. loss	CO_2	Ig. loss	CO_2	Ig. loss
3SSAP	Green	0.37	7.89	0.38	9.77	0.47	10.48	0.47	11.29	0.41	11.85	0.62	12.58
35		.31	1.67	.36	2.70	.49	4.90	.60	5.96	.46	7.05	.58	8.83
35P		.33	2.52	.35	3.10	.38	5.16	.51	5.99	.49	7.35	.57	8.28
35AP		.35	5.43	.42	6.45	.48	7.34	.36	8.59	.86	9.96	1.07	11.67
36		.27	3.51	.25	6.21	.34	8.78	.40	9.02	.84	9.78	.39	10.47
36P		.28	4.14	.32	6.47	.36	8.86	.40	10.16	.68	10.22	.48	11.48
36AP		.40	10.00	.42	10.98	.37	11.38	.44	11.97	.72	12.12	.51	12.91
37		.42	8.84	.32	10.00	.43	11.71	.26	11.82	.43	13.37	.....	.....
37P		.34	9.50	.29	11.81	.25	12.01	.33	12.13	.25	12.44	.79	14.64
38		.19	4.89	.24	5.07	.49	6.51	.49	7.79	.40	10.95	.55	11.69
38P		.25	5.66	.28	6.54	.30	6.65	.28	7.19	.42	8.08	.59	10.12
39		.69	7.55	.54	9.14	.62	10.85	.47	11.12	.48	11.89	1.00	12.63
39P		.59	7.67	.61	9.60	.72	10.82	.57	10.82	.69	11.35	.69	13.39